

## PCT INTERNATIONAL COOPERATION TREATY

PCT

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents  
 United States Patent and Trademark  
 Office  
 Box PCT  
 Washington, D.C.20231  
 ÉTATS-UNIS D'AMÉRIQUE

in its capacity as elected Office

<b>Date of mailing (day/month/year)</b> 02 November 1999 (02.11.99)	
<b>International application No.</b> PCT/GB99/00292	<b>Applicant's or agent's file reference</b> AA 1389 PCT
<b>International filing date (day/month/year)</b> 28 January 1999 (28.01.99)	<b>Priority date (day/month/year)</b> 06 February 1998 (06.02.98)
<b>Applicant</b> ANDREASSON, Anders et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:

04 September 1999 (04.09.99)

☐ in a notice effecting later election filed with the International Bureau on:2. The election ☒ was☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer Marc Salzman Telephone No.: (41-22) 338.83.38
---	--

**THIS PAGE BLANK (USPTO)**

## PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>AA 1389 PCT</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/GB 99/ 00292</b>	International filing date (day/month/year) <b>28/01/1999</b>	(Earliest) Priority Date (day/month/year) <b>06/02/1998</b>
Applicant  <b>JOHNSON MATTHEY PUBLIC LIMITED COMPANY et al.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.



It is also accompanied by a copy of each prior art document cited in this report.

## 1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.



the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :



contained in the international application in written form.



filed together with the international application in computer readable form.



furnished subsequently to this Authority in written form.



furnished subsequently to this Authority in computer readable form.



the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.



the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,



the text is approved as submitted by the applicant.



the text has been established by this Authority to read as follows:

**SYSTEM FOR NOX REDUCTION IN EXHAUST GASES**

5. With regard to the **abstract**,



the text is approved as submitted by the applicant.



the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.



as suggested by the applicant.



because the applicant failed to suggest a figure.



because this figure better characterizes the invention.



None of the figures.

**THIS PAGE BLANK (USPTO)**

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/00292

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B01D53/94 F01N3/28

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B01D F01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 758 713 A (TOYOTA MOTOR CO LTD) 19 February 1997 see column 2, line 34 - column 3, line 22 see column 16, line 33 - column 17, line 55; figure 6	1-4, 7, 9, 10, 12
Y	EP 0 283 913 A (GRACE W R & CO) 28 September 1988 see claims 1-35; figure 1	1-4, 7, 9, 10, 12
A	EP 0 341 832 A (JOHNSON MATTHEY INC) 15 November 1989 see claims 1-10; figure 1	1, 4, 7-9, 11, 12



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

12 May 1999

Date of mailing of the international search report

21/05/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Cubas Alcaraz, J

**THIS PAGE BLANK (USPTO)**

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/00292

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 9710 Derwent Publications Ltd., London, GB; Class H06, AN 97-104299 XP002102630 & JP 08 338320 A (HINO MOTORS LTD) , 24 December 1996 see abstract ---	1,6-8,11
A	DE 40 32 085 A (DIDIER WERKE AG) 16 April 1992 see abstract -----	1

**THIS PAGE BLANK (USPTO)**



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 99/00292

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0758713	A	19-02-1997	JP 9053442 A	25-02-1997
			US 5746989 A	05-05-1998
EP 0283913	A	28-09-1988	US 4912776 A	27-03-1990
			AU 1350988 A	22-09-1988
			DE 3877229 A	18-02-1993
			JP 63236522 A	03-10-1988
EP 0341832	A	15-11-1989	US 4902487 A	20-02-1990
			AT 132940 T	15-01-1996
			DE 68925382 D	22-02-1996
			DE 68925382 T	15-05-1996
			DK 233389 A	14-11-1989
			ES 2081301 T	01-03-1996
			GR 3018800 T	30-04-1996
			IE 71167 B	29-01-1997
			JP 1318715 A	25-12-1989
DE 4032085	A	16-04-1992	BE 1006164 A	31-05-1994
			CH 681429 A	31-03-1993
			DK 171491 A	11-04-1992
			ES 2036473 B	01-03-1994
			IT 1249451 B	23-02-1995

**THIS PAGE BLANK (USPTO)**

From the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

WISHART, Ian Carmichael  
JOHNSON MATTHEY TECHNOLOGY CENTRE  
Blounts Court  
Sonning Common  
Reading RG4 9NH  
GRANDE BRETAGNE

RECEIVED

18 MAY 2000

PCT

NOTIFICATION OF TRANSMITTAL OF  
THE INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT  
(PCT Rule 71.1)

Date of mailing  
(day/month/year)

18.05.00

Applicant's or agent's file reference  
AA 1389 PCT

IMPORTANT NOTIFICATION

International application No.  
PCT/GB99/00292

International filing date (day/month/year)  
28/01/1999

Priority date (day/month/year)  
06/02/1998

Applicant  
JOHNSON MATTHEY PUBLIC LIMITED COMPANY et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/

 European Patent Office  
D-80298 Munich  
Tel. +49 89 2399 - 0 Tx: 523656 epmu d  
Fax: +49 89 2399 - 4465

Authorized officer

Fuerbass, C

Tel. +49 89 2399-8132



**THIS PAGE BLANK (USPTO)**

# PATENT COOPERATION TREATY

## PCT

### INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference <b>AA 1389 PCT</b>	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. <b>PCT/GB99/00292</b>	International filing date (day/month/year) <b>28/01/1999</b>	Priority date (day/month/year) <b>06/02/1998</b>
International Patent Classification (IPC) or national classification and IPC <b>B01D53/94</b>		
Applicant <b>JOHNSON MATTHEY PUBLIC LIMITED COMPANY et al.</b>		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 4 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 9 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand  <b>04/09/1999</b>	Date of completion of this report  <b>18. 05. 00</b>
Name and mailing address of the international preliminary examining authority:   <b>European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465</b>	Authorized officer  <b>Tragoustis, M</b>  Telephone No. <b>+49 89 2399 8623</b>  

**THIS PAGE BLANK (USPTO)**

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB99/00292

## I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

### Description, pages:

1-7 as received on 10/01/2000 with letter of 07/01/2000

### Claims, No.:

1-12 as received on 10/01/2000 with letter of 07/01/2000

### Drawings, sheets:

1/4-4/4 as originally filed

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

**THIS PAGE BLANK (USPTO)**



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/GB99/00292

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

**1. Statement**

Novelty (N)	Yes: Claims 1-12
	No: Claims
Inventive step (IS)	Yes: Claims 1-12
	No: Claims
Industrial applicability (IA)	Yes: Claims 1-12
	No: Claims

**2. Citations and explanations**

**see separate sheet**

**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

**see separate sheet**

**THIS PAGE BLANK (USPTO)**

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

---

International application No. PCT/GB99/00292

The application relates to a SCR system for treating combustion exhaust gas containing NO and particulates.

According to claim 1 the SCR system includes an oxidation catalyst for converting NO to NO<sub>2</sub>, a particulate trap, injection means for injecting a reductant fluid and an SCR catalyst.

By the claimed combination of features the conversion of NO<sub>x</sub> to N<sub>2</sub> is increased and particulate and hydrocarbons are reduced.

D1:EP-A-0283913 discloses a similar apparatus which, however, does not include a particulate trap.

D2:EP-A-0758713 discloses an oxidation catalyst for NO followed by filter trap for carbon particles and by a NO<sub>x</sub> reducing catalyst. The NO<sub>2</sub> produced in the oxidation catalyst is reduced by the trapped carbon to NO which is then reduced by the reducing catalyst to N<sub>2</sub>.

Starting from D2 there is no incentive for the skilled person to introduce a reductant fluid since the NO<sub>2</sub> is reduced by the trapped carbon particles.

Starting from D1 there is also no incentive to install a carbon particulate trap since the NO<sub>2</sub> is reduced by the added reductant fluid.

Thus a combination of the teachings of D1 and D2 would lead the skilled person to either include a carbon particles trap or to add a reductant fluid but not to a combination of both these measures in the claimed manner.

Claims 1-12 meet thus the requirements of Art. 33 PCT.

In claim 1 the wording "at least a portion of NO in the gas stream to NO<sub>2</sub>" should be added after "convert".

**THIS PAGE BLANK (USPTO)**

M 10.11.00

IMPROVEMENTS IN CATALYTIC REDUCTION OF NO<sub>x</sub>

5 The present invention concerns improvements in selective catalytic reduction of NO<sub>x</sub> in waste gas streams such as diesel engine exhausts or other lean exhaust gases such as from gasoline direct injection (GDI).

10 EP 0 758 713 (Toyota) describes a method for purifying the exhaust gas of a diesel engine which uses a catalyst to convert NO in the exhaust gas to NO<sub>2</sub>, thereafter trapping particulate in a filter and oxidising the particulate by reaction with the NO<sub>2</sub>. The exhaust gas is thereafter fed to a NO<sub>x</sub> absorbent or, in one embodiment, to a NO<sub>x</sub> conversion catalyst. Unburnt hydrocarbons and CO in the exhaust gas are trapped in a zeolite and released to react with NO<sub>x</sub> on the NO<sub>x</sub> conversion catalyst.

15 The technique named SCR (Selective Catalytic Reduction) is well established for industrial plant combustion gases, and may be broadly described as passing a hot exhaust gas over a catalyst in the presence of a nitrogenous reductant, especially ammonia or urea. This is effective to reduce the NO<sub>x</sub> content of the exhaust gases by about 20-25% at about 250°C, or possibly rather higher using a platinum catalyst, although platinum catalysts tend to oxidise NH<sub>3</sub> to NO<sub>x</sub> during higher temperature operation. We believe that SCR systems  
20 have been proposed for NO<sub>x</sub> reduction for vehicle engine exhausts, especially large or heavy duty diesel engines, but this does require on-board storage of such reductants, and is not believed to have met with commercial acceptability at this time.

25 We believe that if there could be a significant improvement in performance of SCR systems, they would find wider usage and may be introduced into vehicular applications. It is an aim of the present invention to improve significantly the conversion of NO<sub>x</sub> in a SCR system, and to improve the control of other pollutants using a SCR system.

30 Accordingly, the present invention provides an improved SCR catalyst system for treating combustion exhaust gas containing NO and particulates, comprising in combination and in order, an oxidation catalyst effective to convert NO to NO<sub>2</sub> and enhance the NO<sub>2</sub>

**THIS PAGE BLANK (USP 10)**

content of the exhaust gas, a particulate filter, a source of reductant fluid, injection means for said reductant fluid located downstream of said particulate trap and an SCR catalyst.

5 The invention further provides an improved method of reducing pollutants, including particulates and NO<sub>x</sub> in gas streams, comprising passing such gas stream over an oxidation catalyst under conditions effective to convert at least a portion of NO in the gas stream to NO<sub>2</sub>, and enhance the NO<sub>2</sub> content of the gas stream, removing at least a portion of said particulates in a particulate trap, reacting trapped particulate with NO<sub>2</sub>, adding reductant fluid to the gas stream to form a gas mixture downstream of said trap, and passing the gas  
10 mixture over an SCR catalyst.

Although the present invention provides, at least in its preferred embodiments, the opportunity to reduce very significantly the NO<sub>x</sub> emissions from the lean (high in oxygen) exhaust gases from diesel and similar engines, it is to be noted that the invention also  
15 permits very good reductions in the levels of other regulated pollutants, especially hydrocarbons and particulates.

The invention is believed to have particular application to the exhausts from heavy duty diesel engines, especially vehicle engines, *eg* truck or bus engines, but is not to be  
20 regarded as being limited thereto. Other applications might be LDD (light duty diesel), GDI, CNG (compressed natural gas) engines, ships or stationary sources. For simplicity, however, the majority of this description concerns such vehicle engines.

We have surprisingly found that a "pre-oxidising" step, which is not generally  
25 considered necessary because of the low content of CO and unburnt fuel in diesel exhausts, is particularly effective in increasing the conversion of NO<sub>x</sub> to N<sub>2</sub> by the SCR system. We also believe that minimising the levels of hydrocarbons in the gases may assist in the conversion of NO to NO<sub>2</sub>. This may be achieved catalytically and/or by engine design or management. Desirably, the NO<sub>2</sub>/NO ratio is adjusted according to the present invention to  
30 the most beneficial such ratio for the particular SCR catalyst and CO and hydrocarbons are oxidized prior to the SCR catalyst. Thus, our preliminary results indicate that for a transition

**THIS PAGE BLANK (USPTO)**



metal/zeolite SCR catalyst it is desirable to convert all NO to NO<sub>2</sub>, whereas for a rare earth-based SCR catalyst, a high ratio is desirable providing there is some NO, and for other transition metal-based catalysts gas mixtures are notably better than either substantially only NO or NO<sub>2</sub>. Even more surprisingly, the incorporation of a particulate filter permits still  
5 higher conversions of NO<sub>x</sub>.

The oxidation catalyst may be any suitable catalyst, and is generally available to those skilled in art. For example, a Pt catalyst deposited upon a ceramic or metal through-flow honeycomb support is particularly suitable. Suitable catalysts are e.g. Pt/Al<sub>2</sub>O<sub>3</sub>  
10 catalysts, containing 1-150g Pt/ft<sup>3</sup> (0.035-5.3g Pt/litre) catalyst volume depending on the NO<sub>2</sub>/NO ratio required. Such catalysts may contain other components providing there is a beneficial effect or at least no significant adverse effect.

The source of reductant fluid conveniently uses existing technology to inject fluid  
15 into the gas stream. For example, in the tests for the present invention, a mass controller was used to control supply of compressed NH<sub>3</sub>, which was injected through an annular injector ring mounted in the exhaust pipe. The injector ring had a plurality of injection ports arranged around its periphery. A conventional diesel fuel injection system including pump and injector nozzle has been used to inject urea by the present applicants. A stream of  
20 compressed air was also injected around the nozzle; this provided good mixing and cooling.

The reductant fluid is suitably NH<sub>3</sub>, but other reductant fluids including urea, ammonium carbamate and hydrocarbons including diesel fuel may also be considered. Diesel fuel is, of course, carried on board a diesel-powered vehicle, but diesel fuel itself is  
25 a less selective reductant than NH<sub>3</sub> and is presently not preferred.

Suitable SCR catalysts are available in the art and include Cu-based and vanadia-based catalysts. A preferred catalyst at present is a V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>/TiO<sub>2</sub> catalyst, supported on a honeycomb through-flow support. Although such a catalyst has shown good performance  
30 in the tests described hereafter and is commercially available, we have found that sustained high temperature operation can cause catalyst deactivation. Heavy duty diesel engines,

**THIS PAGE BLANK (USPTO)**

which are almost exclusively turbocharged, can produce exhaust gases at greater than 500°C under conditions of high load and/or high speed, and such temperatures are sufficient to cause catalyst deactivation. In one embodiment of the invention, therefore, cooling means is provided upstream of the SCR catalyst. Cooling means may suitably be activated by sensing high catalyst temperatures or by other, less direct, means, such as determining conditions likely to lead to high catalyst temperatures. Suitable cooling means include water injection upstream of the SCR catalyst, or air injection, for example utilising the engine turbocharger to provide a stream of fresh intake air by-passing the engine. We have observed a loss of activity of the catalyst, however, using water injection, and air injection by modifying the turbocharger leads to higher space velocity over the catalyst which tends to reduce NOx conversion. Preferably, the preferred SCR catalyst is maintained at a temperature from 160°C to 450°C.

We believe that in its presently preferred embodiments, the present invention may depend upon an incomplete conversion of NO to NO<sub>2</sub>. Desirably, therefore, the oxidation catalyst, or the oxidation catalyst together with the particulate trap if used, yields a gas stream entering the SCR catalyst having a ratio of NO to NO<sub>2</sub> of from about 4:1 to about 1:3 by vol, for the commercial vanadia-type catalyst. As mentioned above, other SCR catalysts perform better with different NO/NO<sub>2</sub> ratios. We do not believe that it has previously been suggested to adjust the NO/NO<sub>2</sub> ratio in order to improve NOx reduction.

The present invention incorporates a particulate trap downstream of the oxidation catalyst. We discovered that soot-type particulates may be removed from a particulate trap by "combustion" at relatively low temperatures in the presence of NO<sub>2</sub>. In effect, the incorporation of such a particulate trap serves to clean the exhaust gas of particulates without causing accumulation, with resultant blockage or back-pressure problems, whilst simultaneously reducing a proportion of the NOx. Suitable particulate traps are generally available, and are desirably of the type known as wall-flow filters, generally manufactured from a ceramic, but other designs of particulate trap, including woven, knitted or non-woven heat-resistant fabrics, may be used.

**THIS PAGE BLANK (USPTO)**

It may be desirable to incorporate a clean-up catalyst downstream of the SCR catalyst, to remove any  $\text{NH}_3$  or derivatives thereof which could pass through unreacted or as by-products. Suitable clean-up catalysts are available to the skilled person.

5 A particularly interesting possibility arising from the present invention has especial application to light duty diesel engines (car and utility vehicles) and permits a significant reduction in volume and weight of the exhaust gas after-treatment system, in a suitable engineered system.

10 Several tests have been carried out in making the present invention. These are described below, and are supported by results shown in graphical form in the attached drawings.

15 A commercial 10 litre turbocharged heavy duty diesel engine on a test-bed was used for all the tests described herein.

### Test 1 - (Comparative)

20 A conventional SCR system using a commercial  $\text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2$  catalyst, was adapted and fitted to the exhaust system of the engine.  $\text{NH}_3$  was injected upstream of the SCR catalyst at varying ratios. The  $\text{NH}_3$  was supplied from a cylinder of compressed gas and a conventional mass flow controller used to control the flow of  $\text{NH}_3$  gas to an experimental injection ring. The injection ring was a 10cm diameter annular ring provided with 20 small injection ports arranged to inject gas in the direction of the exhaust gas flow.

25  $\text{NO}_x$  conversions were determined by fitting a  $\text{NO}_x$  analyser before and after the SCR catalyst and are plotted against exhaust gas temperature in Figure 1. Temperatures were altered by maintaining the engine speed constant and altering the torque applied.

30 A number of tests were run at different quantities of  $\text{NH}_3$  injection, from 60% to 100% of theoretical, calculated at 1:1  $\text{NH}_3/\text{NO}$  and 4:3  $\text{NH}_3/\text{NO}_2$ . It can readily be seen that at low temperatures, corresponding to light load, conversions are about 25%, and the highest

**THIS PAGE BLANK (USPTO)**

conversions require stoichiometric (100%) addition of  $\text{NH}_3$  at catalyst temperatures of from 325 to 400°C, and reach about 90%. However, we have determined that at greater than about 70% of stoichiometric  $\text{NH}_3$  injection,  $\text{NH}_3$  slips through the SCR catalyst unreacted, and can cause further pollution problems.

5

## Test 2 (Comparative)

The test rig was modified by inserting into the exhaust pipe upstream of the  $\text{NH}_3$  injection, a commercial platinum oxidation catalyst of 10.5 inch diameter and 6 inch length (26.67cm diameter and 15.24cm length) containing 10g Pt/ft<sup>3</sup> (= 0.35g/litre) of catalyst volume. Identical tests were run, and it was observed from the results plotted in Figure 2, that even at 225°C, the conversion of NOx has increased from 25% to >60%. The greatest conversions were in excess of 95%. No slippage of  $\text{NH}_3$  was observed in this test nor in the following test.

15

## Test 3

The test rig was modified further, by inserting a particulate trap before the  $\text{NH}_3$  injection point, and the tests run again under the same conditions at 100%  $\text{NH}_3$  injection and a space velocity in the range 40,000 to 70,000 hr<sup>-1</sup> over the SCR catalyst. The results are plotted and shown in Figure 3. Surprisingly, there is a dramatic improvement in NOx conversion, to above 90% at 225°C, and reaching 100% at 350°C. Additionally, of course, the particulates which are the most visible pollutant from diesel engines, are also controlled.

20

## Test 4

An R49 test with 80%  $\text{NH}_3$  injection was carried out over a V2O5/WO3/TiO2 SCR catalyst. This gave 67% particulate, 89% HC and 87% NOx conversion; the results are plotted in Figure 4.

30

**THIS PAGE BLANK (USPTO)**



M 10:01:00  
7

Additionally tests have been carried out with a different diesel engine, and the excellent results illustrated in Test 3 and 4 above have been confirmed.

The results have been confirmed also for a non-vanadium SCR catalyst.

**THIS PAGE BLANK (USPTO)**

# CLAIMS

1. An improved SCR system for treating combustion exhaust gas containing NO and particulates, comprising in combination and in order, an oxidation catalyst effective to convert and enhance the NO<sub>2</sub> content of the exhaust gas, a particulate trap, a source of reductant fluid, injections means for such reductant fluid located downstream of said particulate trap and an SCR catalyst.
2. An SCR system according to claim 1, wherein the reductant fluid is NH<sub>3</sub>.
3. An SCR system according to claim 1 or 2, wherein the oxidation catalyst is a platinum catalyst carried on a through-flow honeycomb support.
4. An SCR system according to claims 1,2 or 3 wherein the particulate filter is a wall-flow filter.
5. An SCR system according to any one of the preceding claims, comprising also means to cool gases upstream of the SCR catalyst.
6. An SCR system according to claim 5, comprising also control means such that said gas cooling means is activated only when a high SCR catalyst temperature is detected or conditions are determined that are expected to lead to high catalyst temperatures.
7. A diesel engine provided with an SCR system according to any one of claims 1 to 5.
8. A light duty diesel engine according to claim 6, wherein the volume of the exhaust gas after-treatment system is reduced.
9. A method of reducing pollutants, including particulates and NO<sub>x</sub>, in gas streams, comprising passing such gas stream over an oxidation catalyst under conditions effective to convert at least a portion of NO in the gas stream to NO<sub>2</sub> and enhance the NO<sub>2</sub> content of the

**THIS PAGE BLANK (USPTO)**



**THIS PAGE BLANK (USPTO)**

## PATENT COOPERATION TREATY

PCT

REC'D 22 MAY 2000

IPO

PCT

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference AA 1389 PCT	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/GB99/00292	International filing date (day/month/year) 28/01/1999	Priority date (day/month/year) 06/02/1998
International Patent Classification (IPC) or national classification and IPC B01D53/94		
Applicant JOHNSON MATTHEY PUBLIC LIMITED COMPANY et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 4 sheets, including this cover sheet.

- ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 9 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand  04/09/1999	Date of completion of this report  18.05.00
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer  Tragoustis, M  Telephone No. +49 89 2399 8623 

**THIS PAGE BLANK (USPTO)**



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/GB99/00292

**I. Basis of the report**

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

**Description, pages:**

1-7                      as received on                      10/01/2000    with letter of                      07/01/2000

**Claims, No.:**

1-12                      as received on                      10/01/2000    with letter of                      07/01/2000

**Drawings, sheets:**

1/4-4/4                      as originally filed

2. The amendments have resulted in the cancellation of:

- ☐ the description,              pages:  
☐ the claims,                      Nos.:  
☐ the drawings,                      sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

**THIS PAGE BLANK (USPTO)**

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/GB99/00292

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

**1. Statement**

Novelty (N)	Yes:	Claims	1-12
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-12
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-12
	No:	Claims	

**2. Citations and explanations**

**see separate sheet**

**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

**see separate sheet**

**THIS PAGE BLANK (USPTO)**

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

---

International application No. PCT/GB99/00292

The application relates to a SCR system for treating combustion exhaust gas containing NO and particulates.

According to claim 1 the SCR system includes an oxidation catalyst for converting NO to NO<sub>2</sub>, a particulate trap, injection means for injecting a reductant fluid and an SCR catalyst.

By the claimed combination of features the conversion of NO<sub>x</sub> to N<sub>2</sub> is increased and particulate and hydrocarbons are reduced.

D1:EP-A-0283913 discloses a similar apparatus which, however, does not include a particulate trap.

D2:EP-A-0758713 discloses an oxidation catalyst for NO followed by filter trap for carbon particles and by a NO<sub>x</sub> reducing catalyst. The NO<sub>2</sub> produced in the oxidation catalyst is reduced by the trapped carbon to NO which is then reduced by the reducing catalyst to N<sub>2</sub>.

Starting from D2 there is no incentive for the skilled person to introduce a reductant fluid since the NO<sub>2</sub> is reduced by the trapped carbon particles.

Starting from D1 there is also no incentive to install a carbon particulate trap since the NO<sub>2</sub> is reduced by the added reductant fluid.

Thus a combination of the teachings of D1 and D2 would lead the skilled person to either include a carbon particles trap or to add a reductant fluid but not to a combination of both these measures in the claimed manner.

Claims 1-12 meet thus the requirements of Art. 33 PCT.

In claim 1 the wording "at least a portion of NO in the gas stream to NO<sub>2</sub>" should be added after "convert".

**THIS PAGE BLANK (USPTO)**



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>B01D 53/94, F01N 3/28</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/39809</b> <b>(43) International Publication Date:</b> 12 August 1999 (12.08.99)
<b>(21) International Application Number:</b> PCT/GB99/00292 <b>(22) International Filing Date:</b> 28 January 1999 (28.01.99) <b>(30) Priority Data:</b> 9802504.2                      6 February 1998 (06.02.98)                      GB <b>(71) Applicant (for all designated States except US):</b> JOHNSON MATTHEY PUBLIC LIMITED COMPANY [GB/GB]; 2-4 Cockspur Street, Trafalgar Square, London SW1Y 5BQ (GB). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> ANDREASSON, Anders [SE/SE]; Traneredsvagen 60 A, S-426 77 V. Frolunda (SE). CHANDLER, Guy, Richard [GB/GB]; 48 Harlton Road, Little Eversden, Cambridge CB3 7HB (GB). GOERSMANN, Claus, Friedrich [DE/GB]; 39 Cromwell Road, Cambridge CB1 3EB (GB). WARREN, James, Patrick [GB/GB]; 67 Burnside, Cambridge CB1 3PA (GB). <b>(74) Agent:</b> WISHART, Ian, Carmichael; Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading RG4 9NH (GB).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> SYSTEM FOR NO <sub>x</sub> REDUCTION IN EXHAUST GASES  <b>(57) Abstract</b>  A system for NO <sub>x</sub> reduction in combustion gases, especially from diesel engines, incorporates an oxidation catalyst to convert at least a portion of NO to NO <sub>2</sub> , a particulate filter, a source of reductant such as NH <sub>3</sub> , and an SCR catalyst. Considerable improvements in NO <sub>x</sub> conversion are observed.		

**THIS PAGE BLANK (USPTO)**



**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

**THIS PAGE BLANK (USPTO)**



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification</b> <sup>6</sup> : <b>B01D 53/94, F01N 3/28</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/39809</b> <b>(43) International Publication Date:</b> 12 August 1999 (12.08.99)
<b>(21) International Application Number:</b> PCT/GB99/00292 <b>(22) International Filing Date:</b> 28 January 1999 (28.01.99) <b>(30) Priority Data:</b> 9802504.2                      6 February 1998 (06.02.98)                      GB <b>(71) Applicant (for all designated States except US):</b> JOHNSON MATTHEY PUBLIC LIMITED COMPANY [GB/GB]; 2-4 Cockspur Street, Trafalgar Square, London SW1Y 5BQ (GB). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> ANDREASSON, Anders [SE/SE]; Traneredsvagen 60 A, S-426 77 V. Frolunda (SE). CHANDLER, Guy, Richard [GB/GB]; 48 Harlton Road, Little Eversden, Cambridge CB3 7HB (GB). GO-ERSMANN, Claus, Friedrich [DE/GB]; 39 Cromwell Road, Cambridge CB1 3EB (GB). WARREN, James, Patrick [GB/GB]; 67 Burnside, Cambridge CB1 3PA (GB). <b>(74) Agent:</b> WISHART, Ian, Carmichael; Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading RG4 9NH (GB).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> SYSTEM FOR NO <sub>x</sub> REDUCTION IN EXHAUST GASES  <b>(57) Abstract</b>  A system for NO <sub>x</sub> reduction in combustion gases, especially from diesel engines, incorporates an oxidation catalyst to convert at least a portion of NO to NO <sub>2</sub> , a particulate filter, a source of reductant such as NH <sub>3</sub> , and an SCR catalyst. Considerable improvements in NO <sub>x</sub> conversion are observed.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

SYSTEM FOR NO<sub>x</sub> REDUCTION IN EXHAUST GASES

The present invention concerns improvements in selective catalytic reduction of NO<sub>x</sub> in waste gas streams such as diesel engine exhausts or other lean exhaust gases such as from gasoline direct injection (GDI).

The technique named SCR (Selective Catalytic Reduction) is well established for industrial plant combustion gases, and may be broadly described as passing a hot exhaust gas over a catalyst in the presence of a nitrogenous reductant, especially ammonia or urea. This is effective to reduce the NO<sub>x</sub> content of the exhaust gases by about 20-25% at about 250°C, or possibly rather higher using a platinum catalyst, although platinum catalysts tend to oxidise NH<sub>3</sub> to NO<sub>x</sub> during higher temperature operation. We believe that SCR systems have been proposed for NO<sub>x</sub> reduction for vehicle engine exhausts, especially large or heavy duty diesel engines, but this does require on-board storage of such reductants, and is not believed to have met with commercial acceptability at this time.

We believe that if there could be a significant improvement in performance of SCR systems, they would find wider usage and may be introduced into vehicular applications. It is an aim of the present invention to improve significantly the conversion of NO<sub>x</sub> in a SCR system, and to improve the control of other pollutants using a SCR system.

Accordingly, the present invention provides an improved SCR catalyst system, comprising in combination and in order, an oxidation catalyst effective to convert NO to NO<sub>2</sub>, a particulate filter, a source of reductant fluid and downstream of said source, an SCR catalyst.

The invention further provides an improved method of reducing NO<sub>x</sub> in gas streams containing NO and particulates comprising passing such gas stream over an oxidation catalyst under conditions effective to convert at least a portion of NO in the gas stream to NO<sub>2</sub>, removing at least a portion of said particulates, adding reductant fluid to the gas stream containing enhanced NO<sub>2</sub> to form a gas mixture, and passing the gas mixture over an SCR catalyst.

Although the present invention provides, at least in its preferred embodiments, the opportunity to reduce very significantly the NO<sub>x</sub> emissions from the lean (high in oxygen) exhaust gases from diesel and similar engines, it is to be noted that the invention also permits very good reductions in the levels of other regulated pollutants, especially hydrocarbons and particulates.

The invention is believed to have particular application to the exhausts from heavy duty diesel engines, especially vehicle engines, eg truck or bus engines, but is not to be regarded as being limited thereto. Other applications might be LDD (light duty diesel), GDI, CNG (compressed natural gas) engines, ships or stationary sources. For simplicity, however, the majority of this description concerns such vehicle engines.

We have surprisingly found that a "pre-oxidising" step, which is not generally considered necessary because of the low content of CO and unburnt fuel in diesel exhausts, is particularly effective in increasing the conversion of NO<sub>x</sub> to N<sub>2</sub> by the SCR system. We also believe that minimising the levels of hydrocarbons in the gases may assist in the conversion of NO to NO<sub>2</sub>. This may be achieved catalytically and/or by engine design or management. Desirably, the NO<sub>2</sub>/NO ratio is adjusted according to the present invention to the most beneficial such ratio for the particular SCR catalyst and CO and hydrocarbons are oxidized prior to the SCR catalyst. Thus, our preliminary results indicate that for a transition metal/zeolite SCR catalyst it is desirable to convert all NO to NO<sub>2</sub>, whereas for a rare earth-based SCR catalyst, a high ratio is desirable providing there is some NO, and for other transition metal-based catalysts gas mixtures are notably better than either substantially only NO or NO<sub>2</sub>. Even more surprisingly, the incorporation of a particulate filter permits still higher conversions of NO<sub>x</sub>.

The oxidation catalyst may be any suitable catalyst, and is generally available to those skilled in art. For example, a Pt catalyst deposited upon a ceramic or metal through-flow honeycomb support is particularly suitable. Suitable catalysts are e.g. Pt/Al<sub>2</sub>O<sub>3</sub> catalysts, containing 1-150g Pt/ft<sup>3</sup> (0.035-5.3g Pt/litre) catalyst volume depending on the

NO<sub>2</sub>/NO ratio required. Such catalysts may contain other components providing there is a beneficial effect or at least no significant adverse effect.

5 The source of reductant fluid conveniently uses existing technology to inject fluid into the gas stream. For example, in the tests for the present invention, a mass controller was used to control supply of compressed NH<sub>3</sub>, which was injected through an annular injector ring mounted in the exhaust pipe. The injector ring had a plurality of injection ports arranged around its periphery. A conventional diesel fuel injection system including pump and injector nozzle has been used to inject urea by the present applicants. A stream of  
10 compressed air was also injected around the nozzle; this provided good mixing and cooling.

The reductant fluid is suitably NH<sub>3</sub>, but other reductant fluids including urea, ammonium carbamate and hydrocarbons including diesel fuel may also be considered. Diesel fuel is, of course, carried on board a diesel-powered vehicle, but diesel fuel itself is  
15 a less selective reductant than NH<sub>3</sub> and is presently not preferred.

Suitable SCR catalysts are available in the art and include Cu-based and vanadia-based catalysts. A preferred catalyst at present is a V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>/TiO<sub>2</sub> catalyst, supported on a honeycomb through-flow support. Although such a catalyst has shown good performance  
20 in the tests described hereafter and is commercially available, we have found that sustained high temperature operation can cause catalyst deactivation. Heavy duty diesel engines, which are almost exclusively turbocharged, can produce exhaust gases at greater than 500°C under conditions of high load and/or high speed, and such temperatures are sufficient to cause catalyst deactivation. In one embodiment of the invention, therefore, cooling means  
25 is provided upstream of the SCR catalyst. Cooling means may suitably be activated by sensing high catalyst temperatures or by other, less direct, means, such as determining conditions likely to lead to high catalyst temperatures. Suitable cooling means include water injection upstream of the SCR catalyst, or air injection, for example utilising the engine turbocharger to provide a stream of fresh intake air by-passing the engine. We have  
30 observed a loss of activity of the catalyst, however, using water injection, and air injection by modifying the turbocharger leads to higher space velocity over the catalyst which tends

to reduce NO<sub>x</sub> conversion. Preferably, the preferred SCR catalyst is maintained at a temperature from 160°C to 450°C.

We believe that in its presently preferred embodiments, the present invention may  
5 depend upon an incomplete conversion of NO to NO<sub>2</sub>. Desirably, therefore, the oxidation catalyst, or the oxidation catalyst together with the particulate trap if used, yields a gas stream entering the SCR catalyst having a ratio of NO to NO<sub>2</sub> of from about 4:1 to about 1:3 by vol, for the commercial vanadia-type catalyst. As mentioned above, other SCR catalysts perform better with different NO/NO<sub>2</sub> ratios. We do not believe that it has previously been  
10 suggested to adjust the NO/NO<sub>2</sub> ratio in order to improve NO<sub>x</sub> reduction.

The present invention incorporates a particulate trap downstream of the oxidation catalyst. We discovered that soot-type particulates may be removed from a particulate trap by "combustion" at relatively low temperatures in the presence of NO<sub>2</sub>. In effect, the  
15 incorporation of such a particulate trap serves to clean the exhaust gas of particulates without causing accumulation, with resultant blockage or back-pressure problems, whilst simultaneously reducing a proportion of the NO<sub>x</sub>. Suitable particulate traps are generally available, and are desirably of the type known as wall-flow filters, generally manufactured from a ceramic, but other designs of particulate trap, including woven knitted or non-woven  
20 heat-resistant fabrics, may be used.

It may be desirable to incorporate a clean-up catalyst downstream of the SCR catalyst, to remove any NH<sub>3</sub> or derivatives thereof which could pass through unreacted or as by-products. Suitable clean-up catalysts are available to the skilled person.

25

A particularly interesting possibility arising from the present invention has especial application to light duty diesel engines (car and utility vehicles) and permits a significant reduction in volume and weight of the exhaust gas after-treatment system, in a suitable engineered system.

30



Several tests have been carried out in making the present invention. These are described below, and are supported by results shown in graphical form in the attached drawings.

- 5           A commercial 10 litre turbocharged heavy duty diesel engine on a test-bed was used for all the tests described herein.

#### Test 1 - (Comparative)

- 10           A conventional SCR system using a commercial  $V_2O_5/WO_3/TiO_2$  catalyst, was adapted and fitted to the exhaust system of the engine.  $NH_3$  was injected upstream of the SCR catalyst at varying ratios. The  $NH_3$  was supplied from a cylinder of compressed gas and a conventional mass flow controller used to control the flow of  $NH_3$  gas to an experimental injection ring. The injection ring was a 10cm diameter annular ring provided  
15 with 20 small injection ports arranged to inject gas in the direction of the exhaust gas flow.  $NO_x$  conversions were determined by fitting a  $NO_x$  analyser before and after the SCR catalyst and are plotted against exhaust gas temperature in Figure 1. Temperatures were altered by maintaining the engine speed constant and altering the torque applied.

- 20           A number of tests were run at different quantities of  $NH_3$  injection, from 60% to 100% of theoretical, calculated at 1:1  $NH_3/NO$  and 4:3  $NH_3/NO_2$ . It can readily be seen that at low temperatures, corresponding to light load, conversions are about 25%, and the highest conversions require stoichiometric (100%) addition of  $NH_3$  at catalyst temperatures of from 325 to 400°C, and reach about 90%. However, we have determined that at greater than  
25 about 70% of stoichiometric  $NH_3$  injection,  $NH_3$  slips through the SCR catalyst unreacted, and can cause further pollution problems.

#### Test 2 (Comparative)

- 30           The test rig was modified by inserting into the exhaust pipe upstream of the  $NH_3$  injection, a commercial platinum oxidation catalyst of 10.5 inch diameter and 6 inch length

(26.67cm diameter and 15.24cm length) containing 10g Pt/ft<sup>3</sup> (= 0.35g/litre) of catalyst volume. Identical tests were run, and it was observed from the results plotted in Figure 2, that even at 225°C, the conversion of NOx has increased from 25% to >60%. The greatest conversions were in excess of 95%. No slippage of NH<sub>3</sub> was observed in this test nor in the following test.

### **Test 3**

The test rig was modified further, by inserting a particulate trap before the NH<sub>3</sub> injection point, and the tests run again under the same conditions at 100% NH<sub>3</sub> injection and a space velocity in the range 40,000 to 70,000 hr<sup>-1</sup> over the SCR catalyst. The results are plotted and shown in Figure 3. Surprisingly, there is a dramatic improvement in NOx conversion, to above 90% at 225°C, and reaching 100% at 350°C. Additionally, of course, the particulates which are the most visible pollutant from diesel engines, are also controlled.

### **Test 4**

An R49 test with 80% NH<sub>3</sub> injection was carried out over a V<sub>2</sub>O<sub>5</sub>/WO<sub>3</sub>/TiO<sub>2</sub> SCR catalyst. This gave 67% particulate, 89% HC and 87% NOx conversion; the results are plotted in Figure 4.

Additionally tests have been carried out with a different diesel engine, and the excellent results illustrated in Test 3 and 4 above have been confirmed.

The results have been confirmed also for a non-vanadium SCR catalyst.

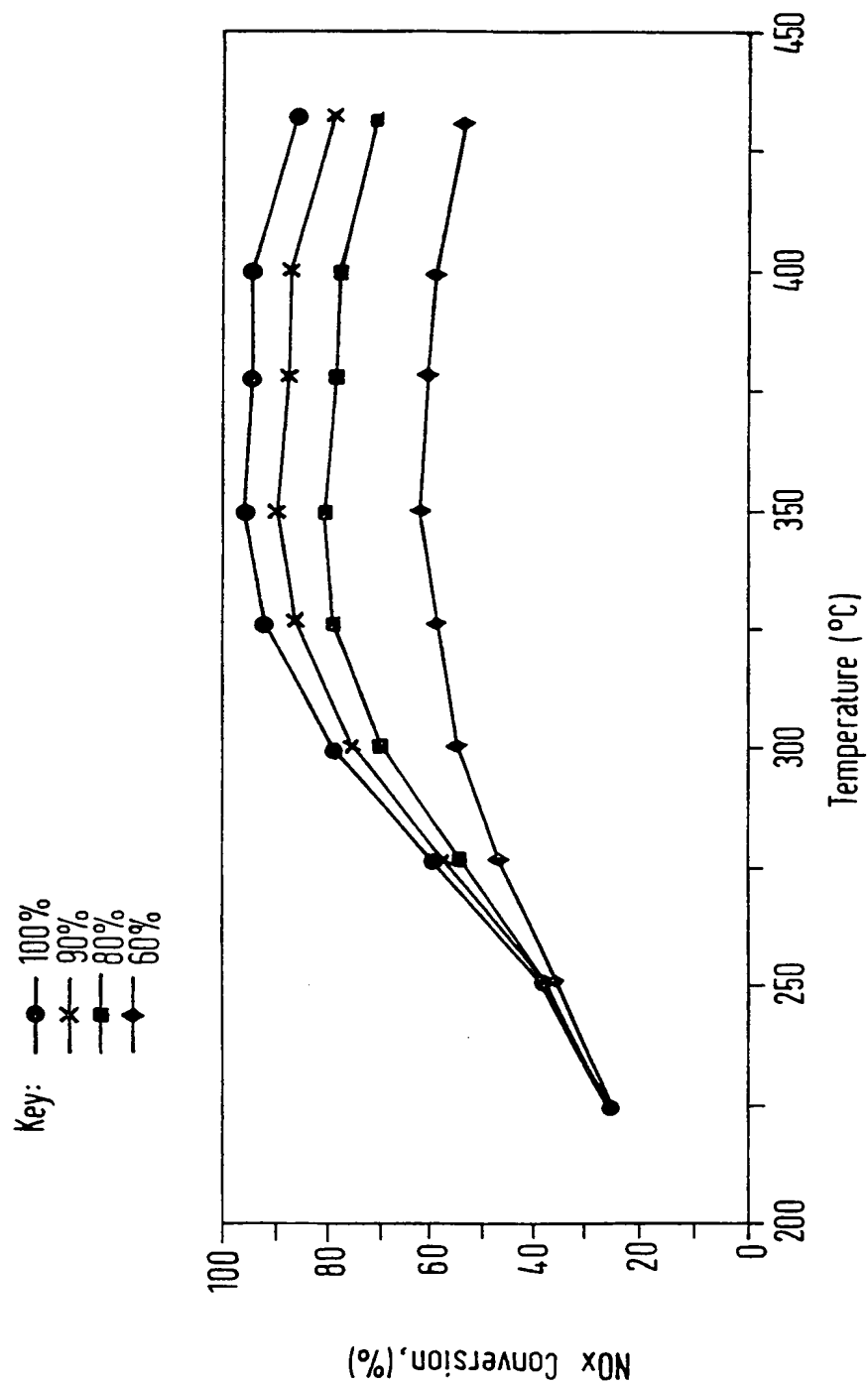
CLAIMS

1. An improved SCR system for treating combustion exhaust gas containing NO and particulates, comprising in combination and in order, an oxidation catalyst effective to  
5 convert at least a portion of NO in said NO<sub>x</sub> to NO<sub>2</sub>, a particulate trap, a source of reductant fluid and an SCR catalyst.
2. An SCR system according to claim 1, wherein the reductant fluid is NH<sub>3</sub>.
- 10 3. An SCR system according to claim 1 or 2, wherein the oxidation catalyst is a platinum catalyst carried on a through-flow honeycomb support.
4. An SCR system according to claims 1,2 or 3 wherein the particulate filter is a wall-flow filter.
- 15 5. An SCR system according to any one of the preceding claims, comprising also means to cool gases upstream of the SCR catalyst.
6. An SCR system according to claim 5, comprising also control means such that said  
20 gas cooling means is activated only when a high SCR catalyst temperature is detected or conditions are determined that are expected to lead to high catalyst temperatures.
7. A diesel engine provided with an SCR system according to any one of claims 1 to 5.
- 25 8. A light duty diesel engine according to claim 6, wherein the volume of the exhaust gas after-treatment system is reduced.
9. A method of reducing pollutants, including particulates and NO<sub>x</sub>, in gas streams, comprising passing such gas stream over an oxidation catalyst under conditions effective to  
30 convert at least a portion of NO in the gas stream to NO<sub>2</sub>, removing at least a portion of said

particulates, adding reductant fluid to the gas stream containing enhanced NO<sub>2</sub> to form a gas mixture, and passing the gas mixture over an SCR catalyst under NO<sub>x</sub> reduction conditions.

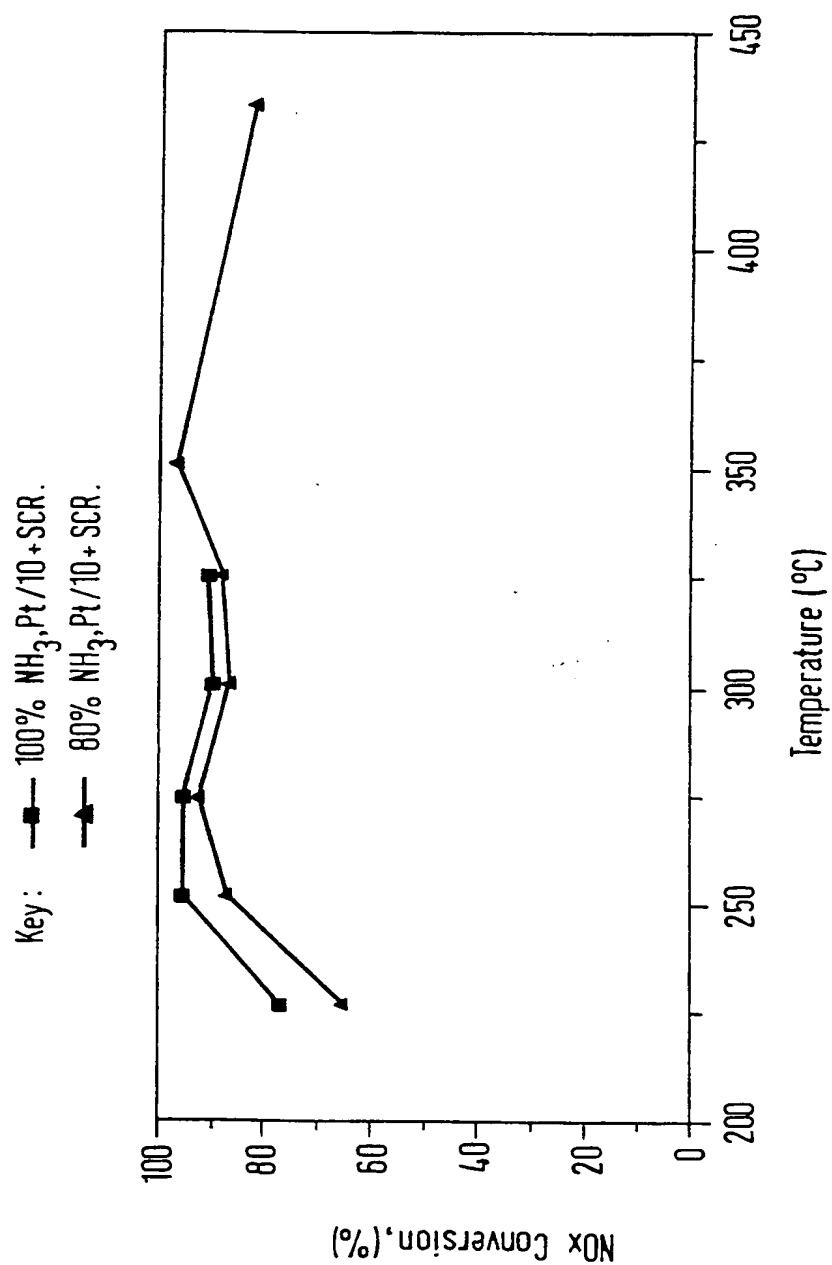
10. A method according to claim 9, wherein said gas stream is the exhaust from a diesel,  
5 GDI or CNG engine.
11. A method according to claim 9 or 10, wherein the gases are cooled, if necessary,  
before reaching the SCR catalyst.
- 10 12. A method according to claim 9, 10 or 11, wherein the NO to NO<sub>2</sub> ratio in the gases  
is adjusted to a level pre-determined to be optimum for the SCR catalyst, by oxidation of NO  
over an oxidation catalyst.

1/4



**THIS PAGE BLANK (USPTO)**

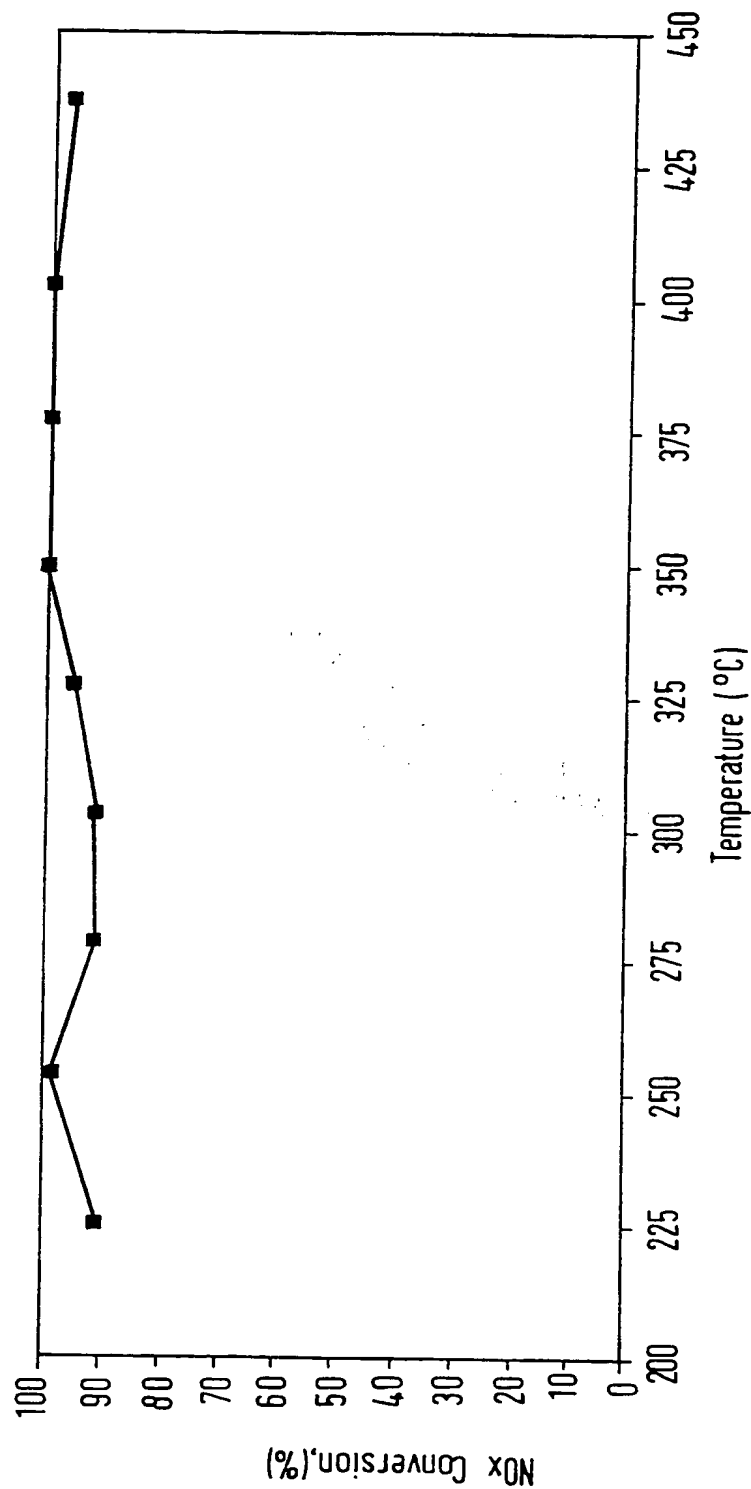
2/4



**THIS PAGE BLANK (USPTO)**

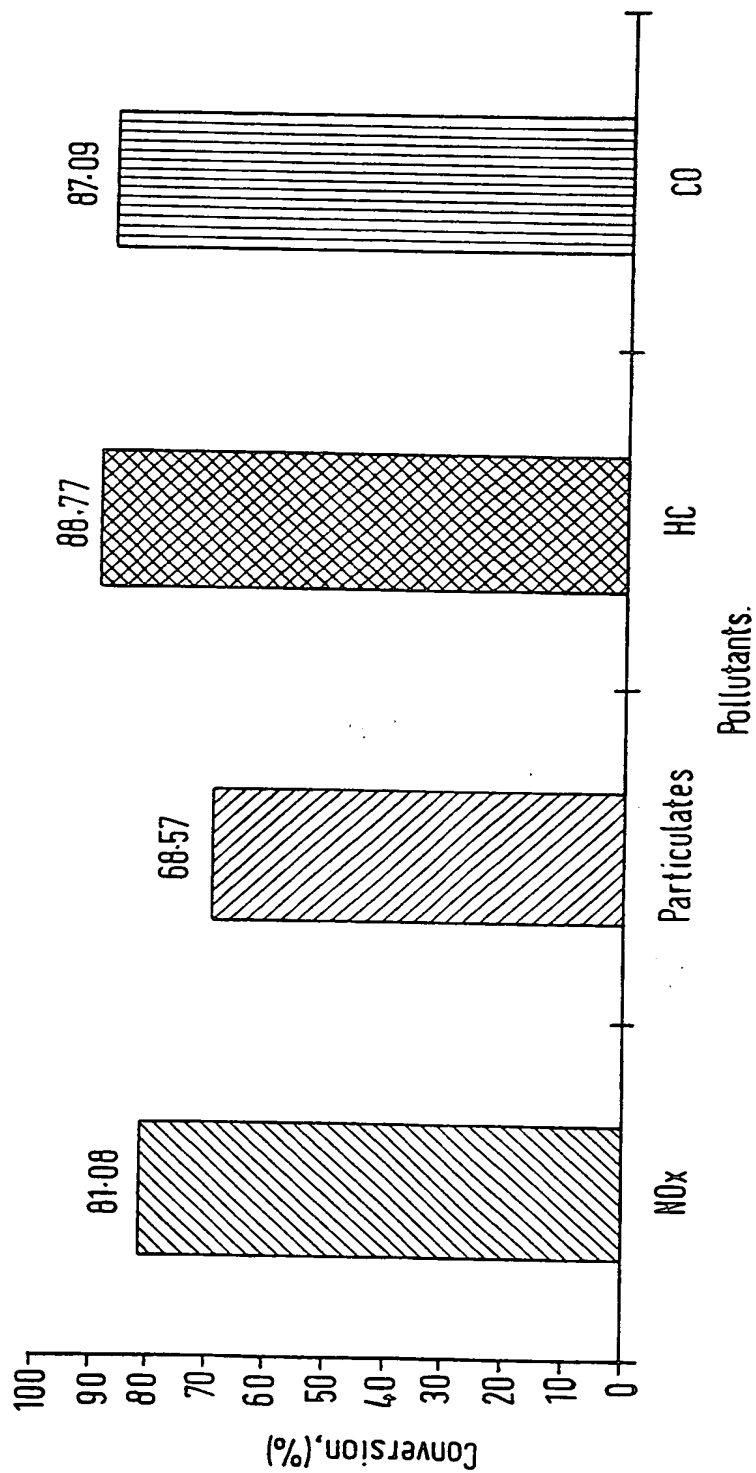


3/4



**THIS PAGE BLANK (USPTO)**

4/4



**THIS PAGE BLANK (USPTO)**